# *Electrodeposition of nanomaterials*

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# Report Documentation Page

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# *Introduction:*

Electrodeposition

- has long history

Miniature mask from Loma Negra, Moche culture, northern Peru: 100 B.C. – 800 A.D.

Au applied to Cu by displacement plating.

*From: 'Pre-Columbian Surface Metallurgy', H. Lechtman, Sci. Am. (1984).*

# *Introduction:*

Electrodeposition

- has long history
- is an important current technology

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# Metal interconnects in ultra large scale integrated circuits

Cu interconnects on IBM chip

- electrodeposited Cu has replaced Al in ULSI
- higher conductivity – better electromigration resistance

*P. C. Andricacos, Interface,* ***8****(1) (1999).*

# *Introduction:*

Electrodeposition

- has long history
- is an important current technology
- will play pivotal role in nanofabrication

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## *Topics:*

- Controlling morphology
- The dual-damascene method
- Electroless deposition
- Multilayer electrodeposition

*Topics:*

- Controlling morphology
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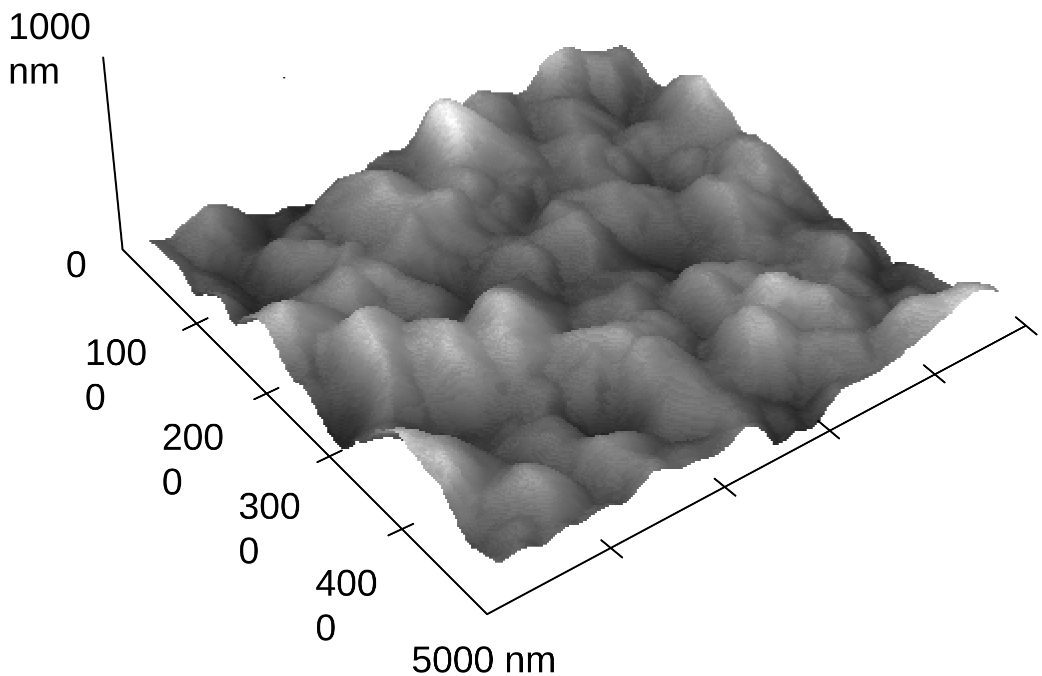
# Why do electrodeposited thin films become rough?




AFM image of film electrodeposited from 0.3M $CuSO_4$ / 1.2M $H_2SO_4$, 4 mA $cm^{-2}$, *t=6 mins*

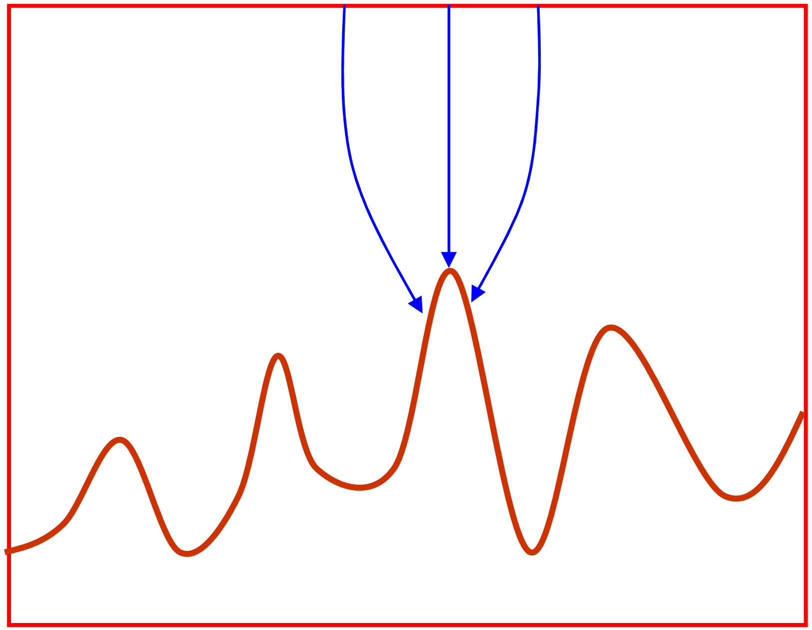
- Random fluctuations → noise
- Surface tension leads to smoothening

$$\mu = \mu_{eq} + \Gamma \kappa v_m$$

- Can incorporate these ideas in equation of motion for surface e.g.

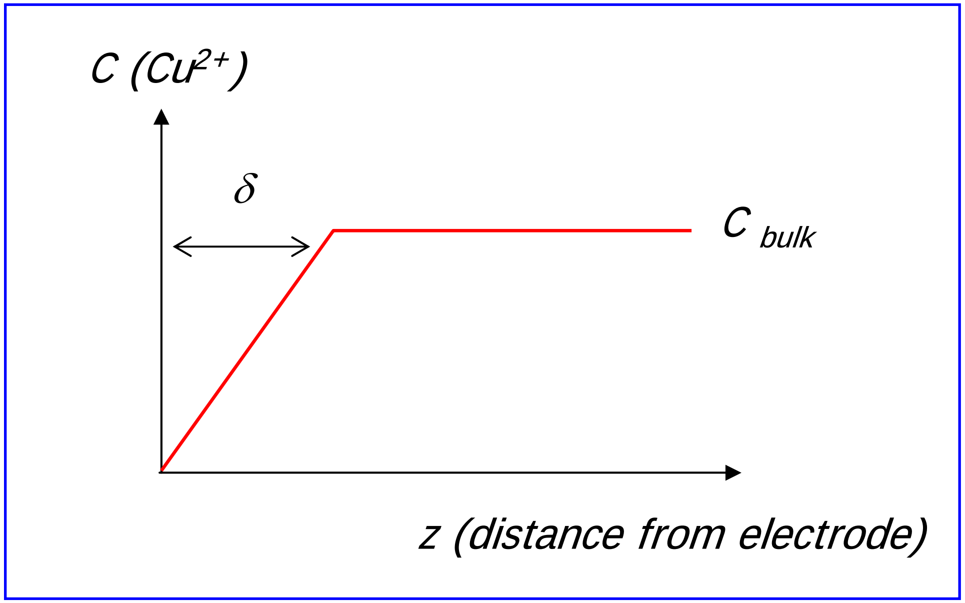
$$\partial h(\mathbf{x},t) / \partial t = -c\nabla^4 h(\mathbf{x},t) + \eta(\mathbf{x},t)$$

- Mass transport is by diffusion → *Laplacian instability*



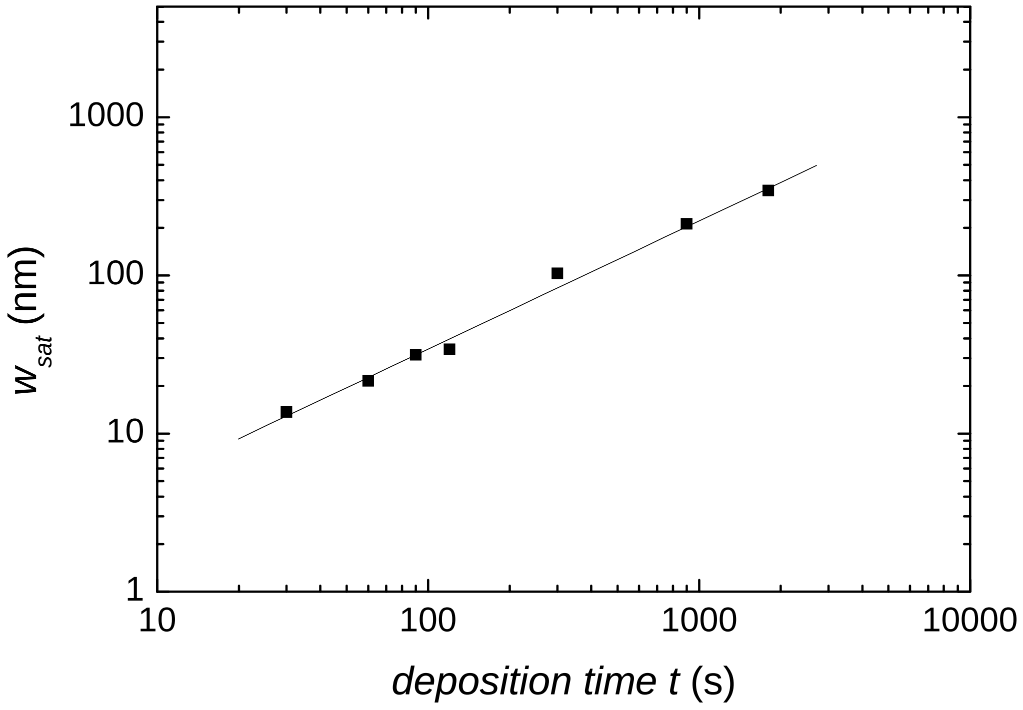
Peaks grow faster than valleys

# Further consequences of diffusion:




- Diffusion limited current $\propto -D\dfrac{C_{bulk}}{\delta}$
- $\delta$ depends on convection

# Complex non-linear system *but* simple power law behaviour (scaling)




- *Local* roughness scales as $t^{\beta_{loc}}$
- *Large-scale* roughness ($w_{sat}$) scales as $t^{\beta+\beta_{loc}}$

- Can change current density, electrolyte concentration, temperature

- Only $\beta_{loc}$ changes.

- $\beta_{loc}$ depends on ratio of current to diffusion-limited current – Laplacian instability

*S. Huo and W. Schwarzacher, Phys. Rev. Lett.* ***86****, 256 (2001)*

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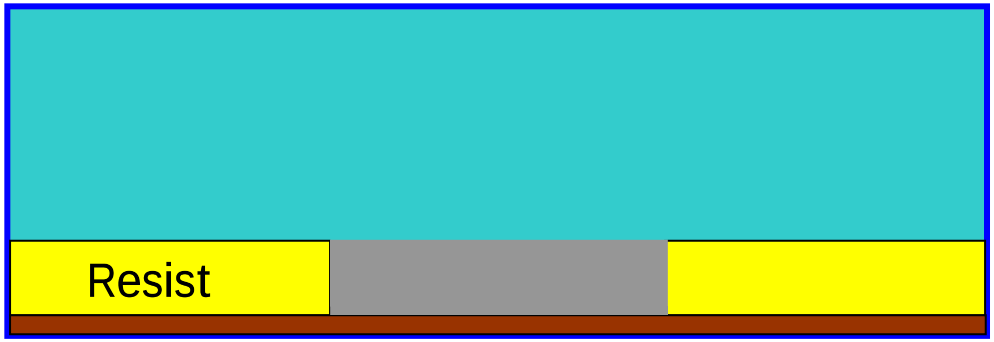
*This is a useful result:*

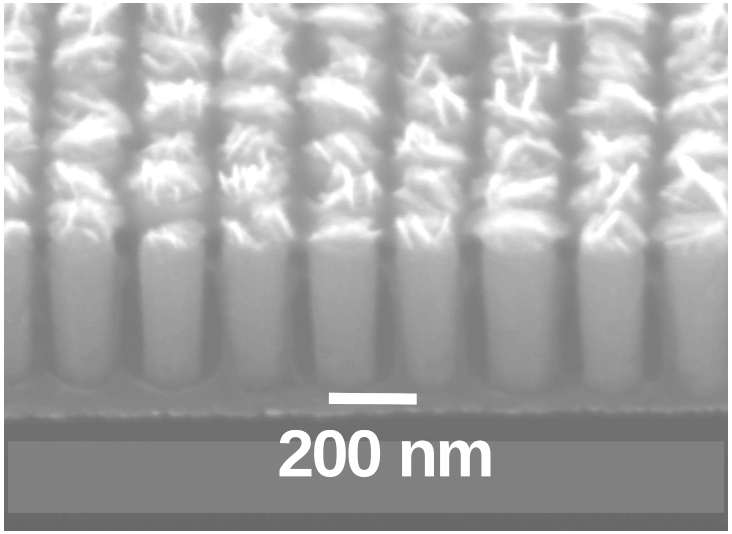
- Only 5 numbers (scaling exponents and pre-factors) needed to describe roughness on any length-scale of film of any thickness
- 2 are invariant, 2 can be determined from a single film.

# Example: deposition on patterned electrodes




- selective method
- widely used in microfabrication ('through-mask plating')

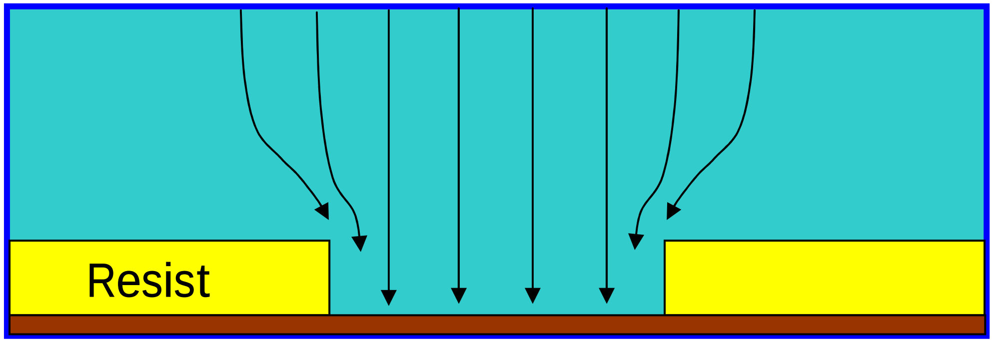
# Example: deposition on patterned electrodes




Electrodeposited Co-Ni alloy pillars for patterned media studies.  Patterning used interference lithography.

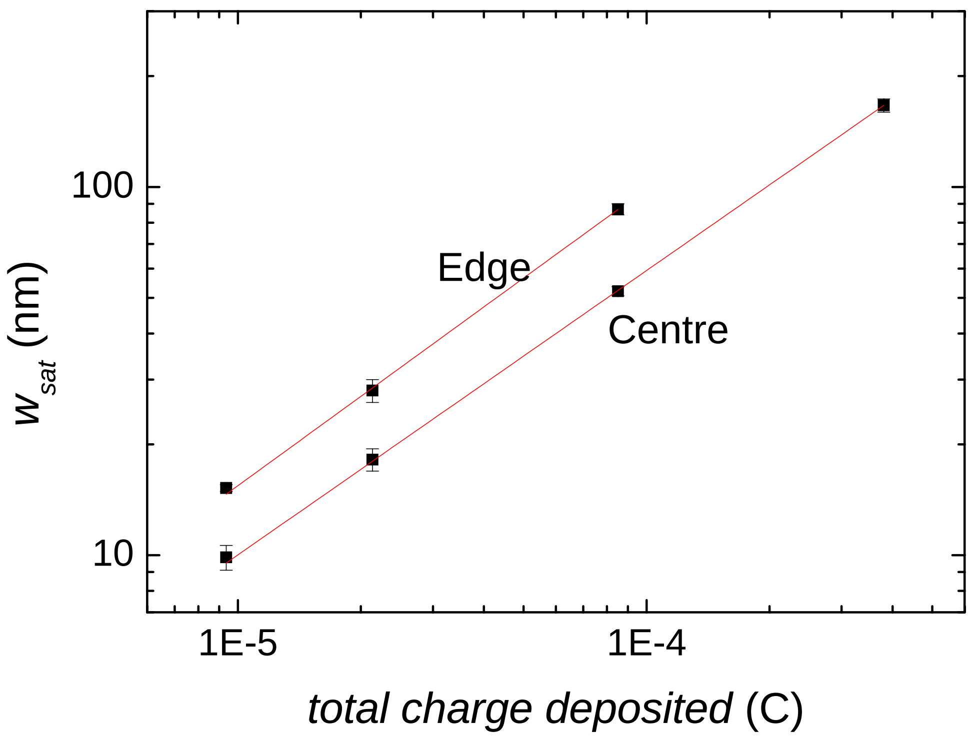
*(Collaboration with C. A. Ross et al., M.I.T.)*

# Example: deposition on patterned electrodes




- edge → greater current density
- what happens to roughness?

- Edge significantly rougher than centre:



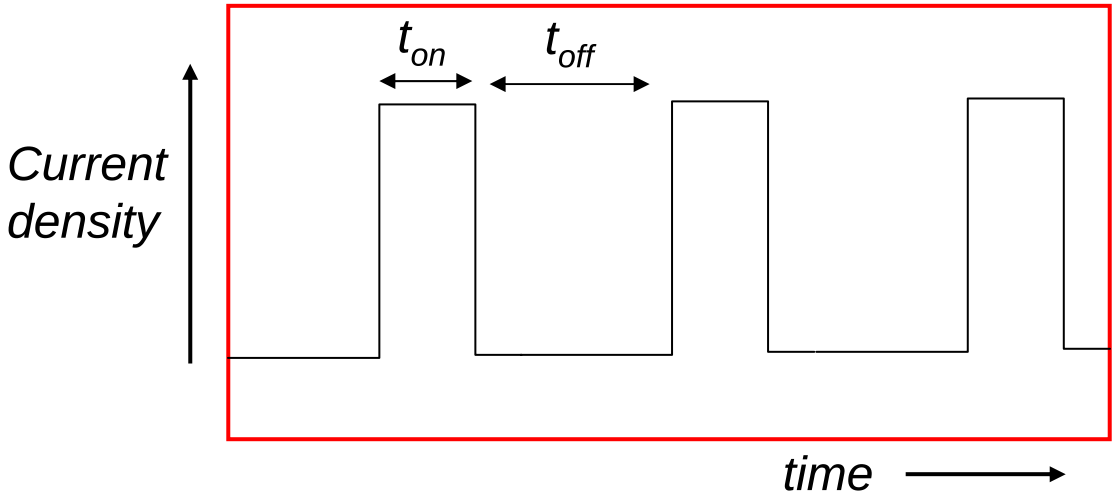

- *but* same scaling exponent $\beta+\beta_{loc}$

*R. Cecchini, J. J. Mallett and W. Schwarzacher*

*(Electrochem. Sol. State Lett., in press)*

# *Tools for controlling morphology:*

- Pulse electrodeposition




- High current density for ‘on’-pulse → high nucleation density
- Complexing agents and additives

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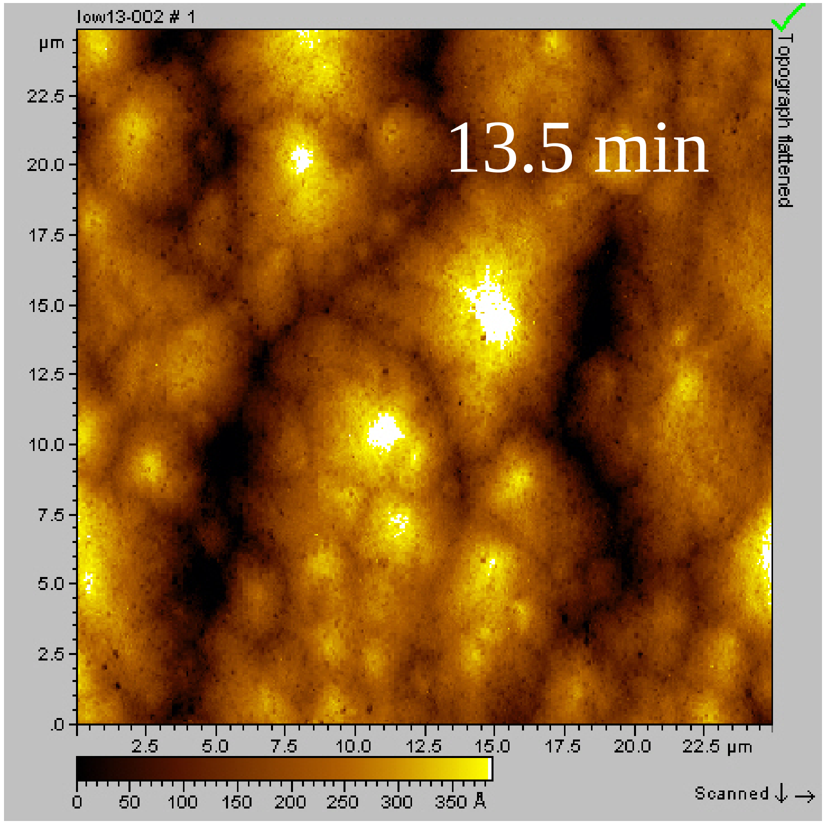
# *Influence of additives*

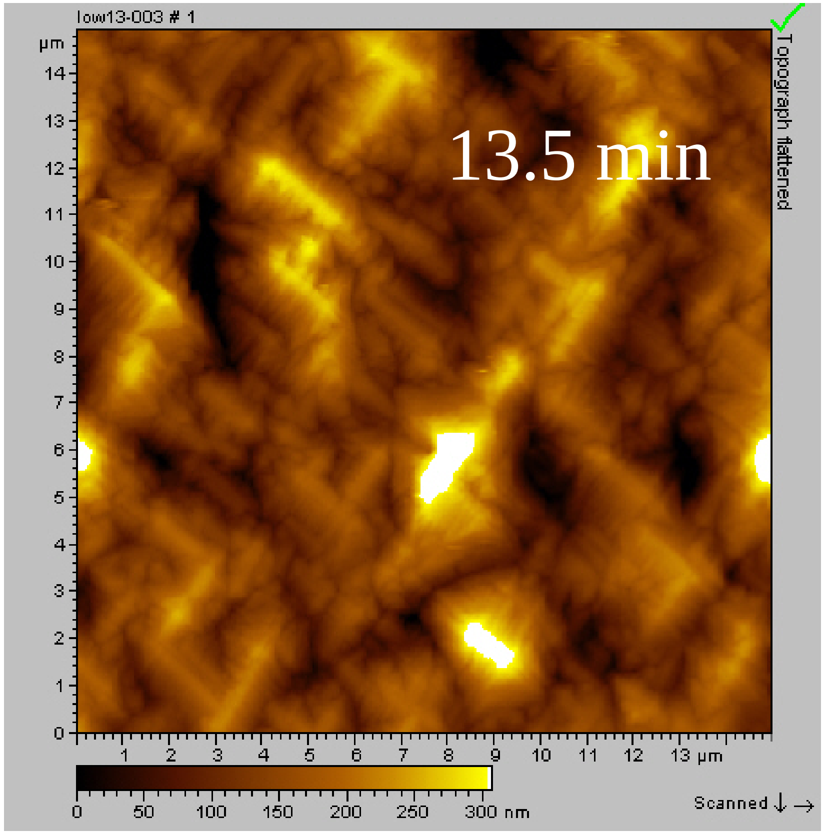
- When textured substrate used, $Cl^-$ has major effect




Cu-on-Si substrate
No $Cl^-$

# *Influence of additives*

- When textured substrate used, $Cl^-$ has major effect




Cu-on-Si substrate
0.25mM Cl

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*Topics:*

- Controlling morphology
- The dual-damascene method
- Electroless deposition
- Multilayer electrodeposition

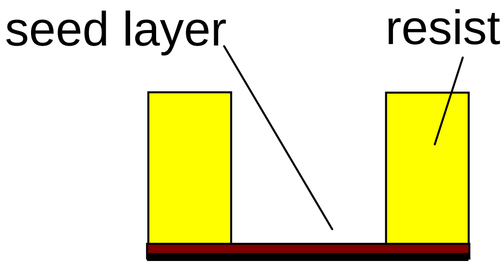
# Metal interconnects in ultra large scale integrated circuits

Cu interconnects on IBM chip

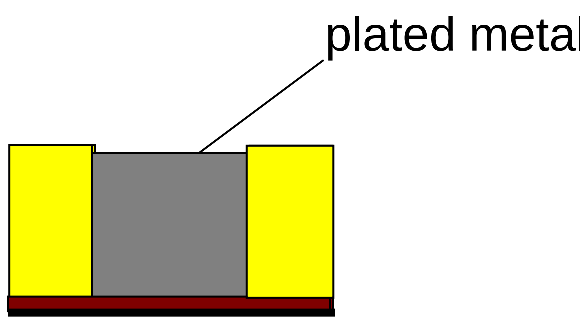
- electrodeposited Cu has replaced Al in ULSI
- higher conductivity – better electromigration resistance

*P. C. Andricacos, Interface,* ***8****(1) (1999).*

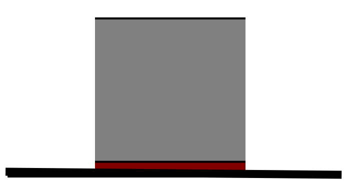
## Through-mask plating




1 patterning

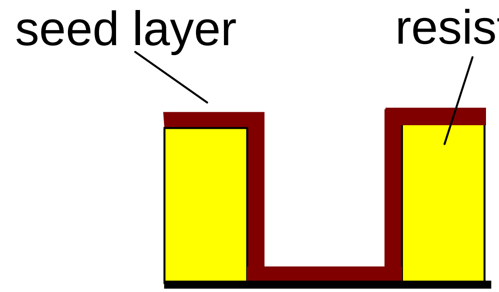



2 electrodeposition

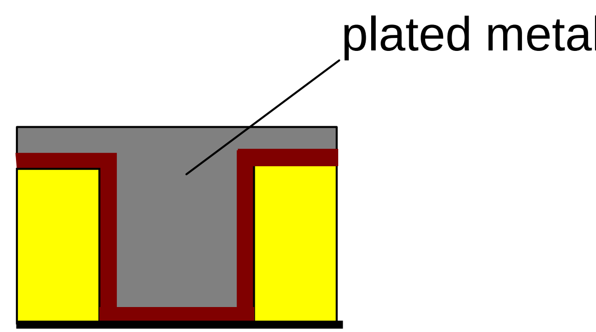


3 seed layer etching

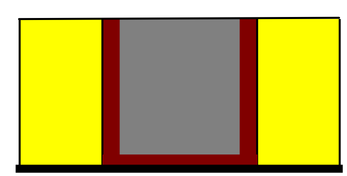
## Damascene plating




1 patterning

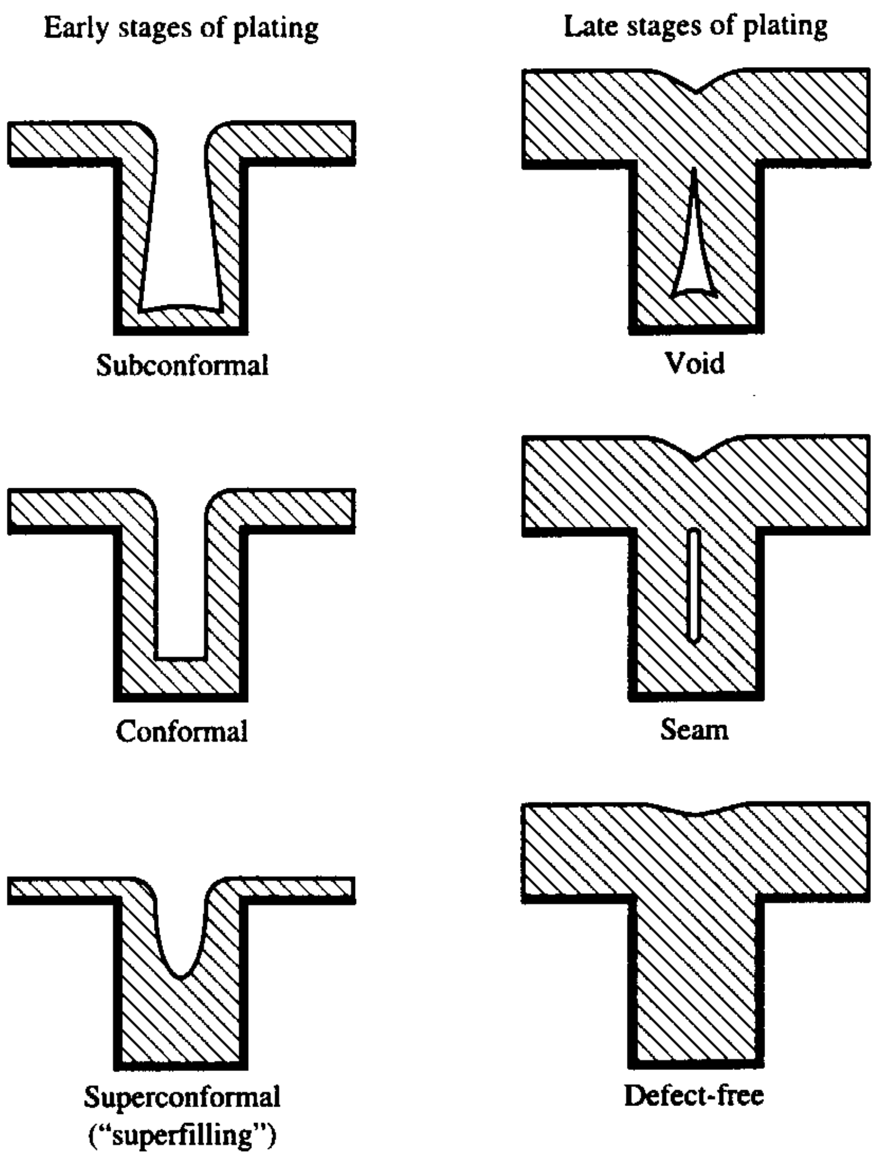



2 electrodeposition

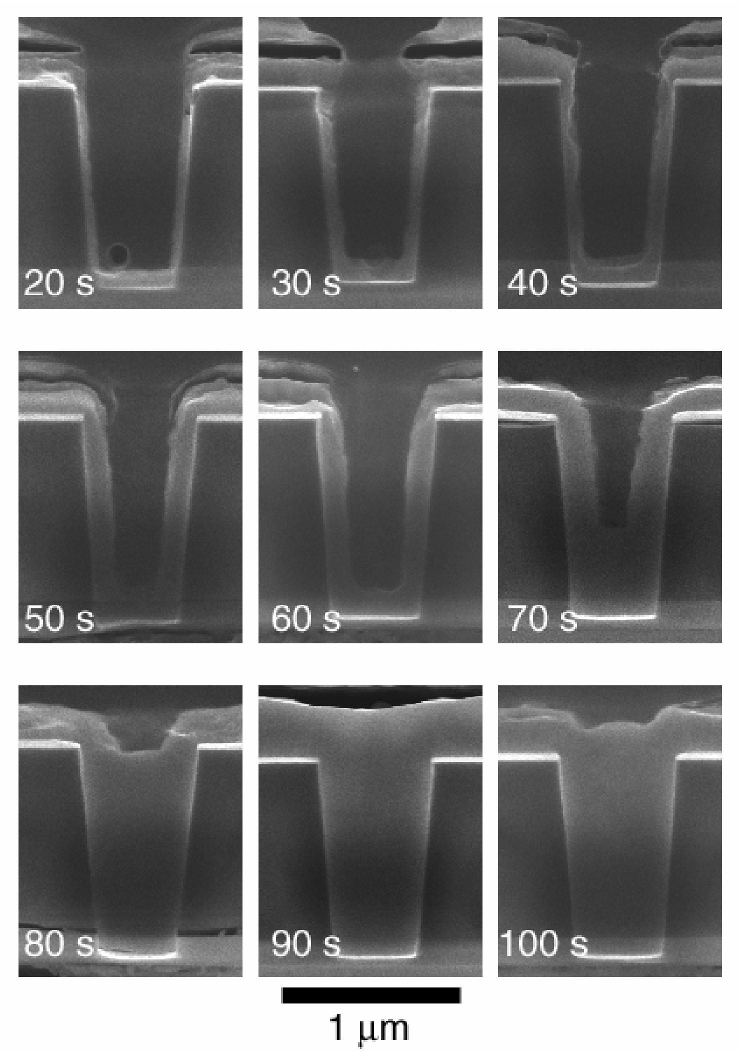


3 planarization

# ‘Superfilling’ needed to avoid defects



# Requires appropriate additives

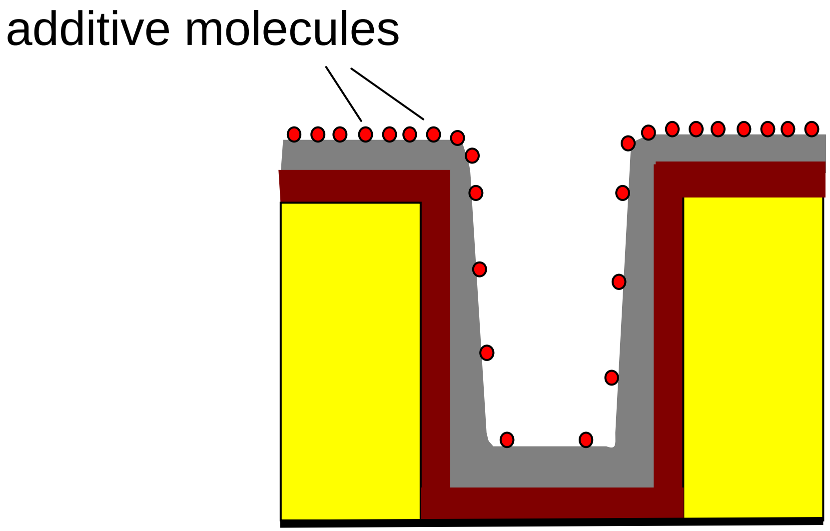



- 1.8 M $H_2SO_4$
- 0.25 M $CuSO_4$
- 1 mM NaCl
- 88 $\mu$M PEG ($M_w$=3,400) n=77
- ~ 5 $\mu$M SPS/MPSA

D. Josell, B. Baker, D. Wheeler, C. Witt and T.P. Moffat,
J. Electrochem. Soc. **149**, C637 (2002).

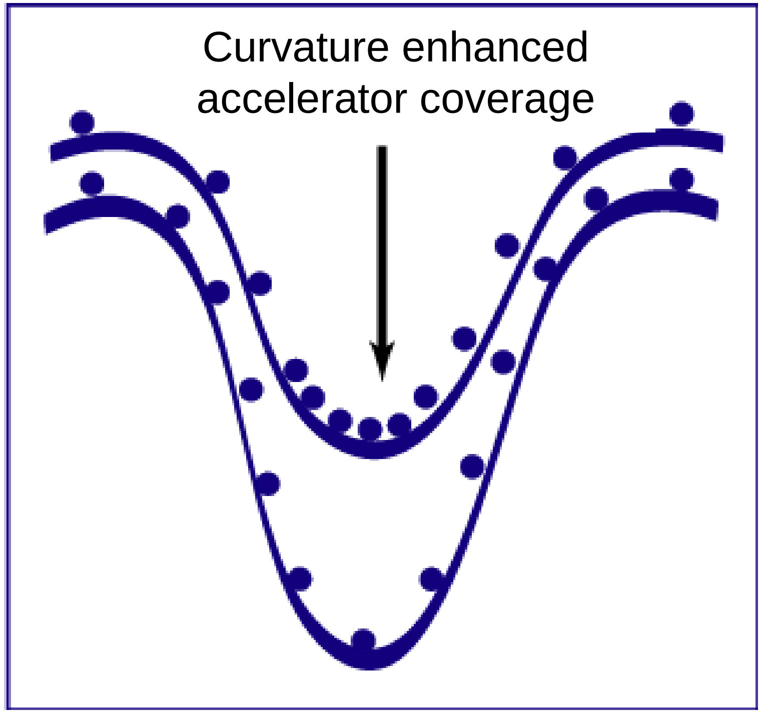
## Simple model:

- Additives act to block deposition
- Additive diffusion to recesses slow




*Unfortunately this model is wrong!*

# Curvature Enhanced Accelerator Coverage Mechanism

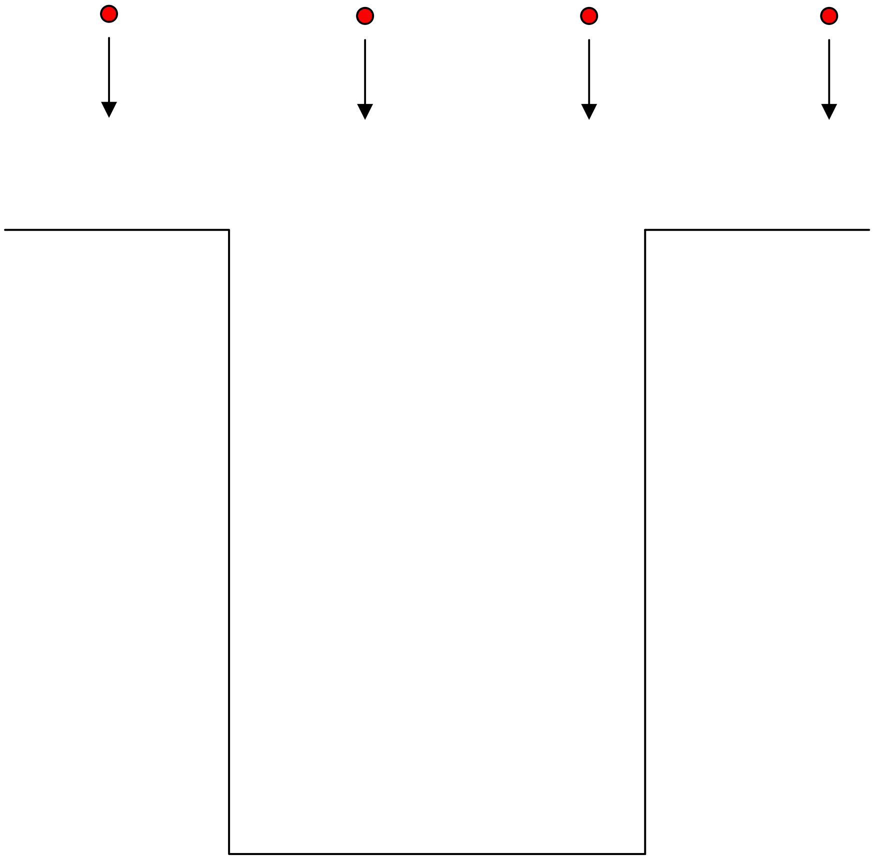



- Metal deposition rate *increases* with catalyst coverage
- Local catalyst coverage increases as local area decreases - converse also true.

T.P. Moffat, D. Wheeler, W.H. Huber and D. Josell,
Electrochemical and Solid-State Letters **4**, C26 (2001).

# Curvature Enhanced Accelerator Coverage Mechanism

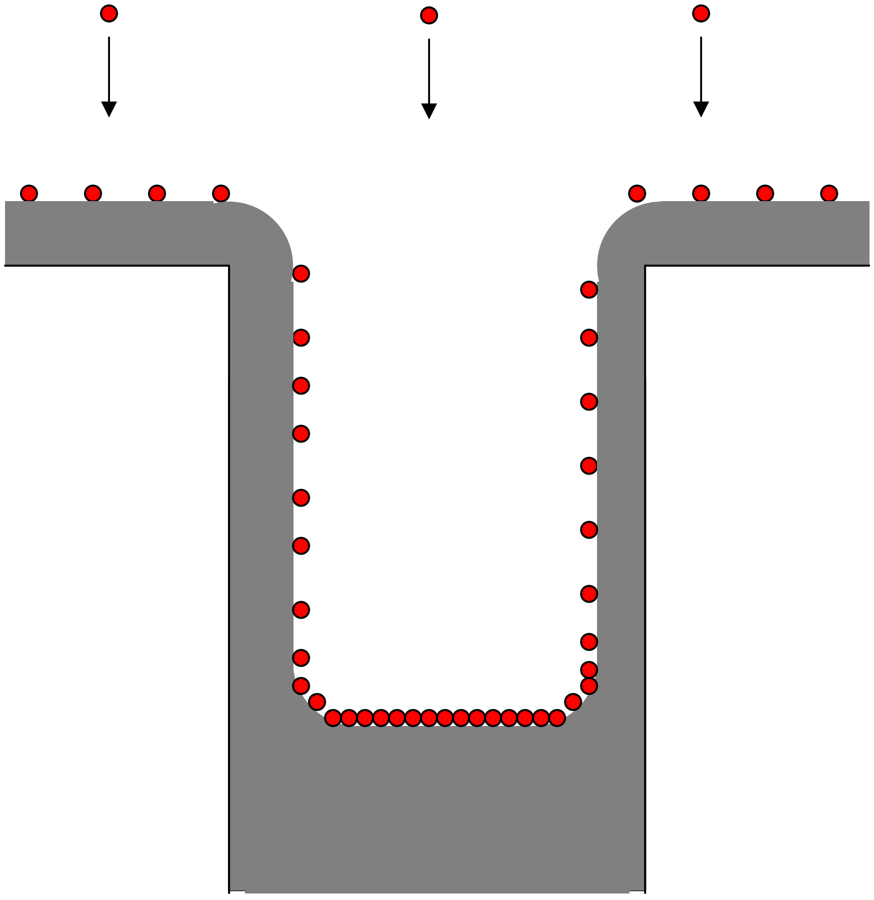
- Initial condition - catalyst coverage $\theta = 0$
- Catalyst accumulates from reaction with precursors in electrolyte



# Curvature Enhanced Accelerator Coverage Mechanism

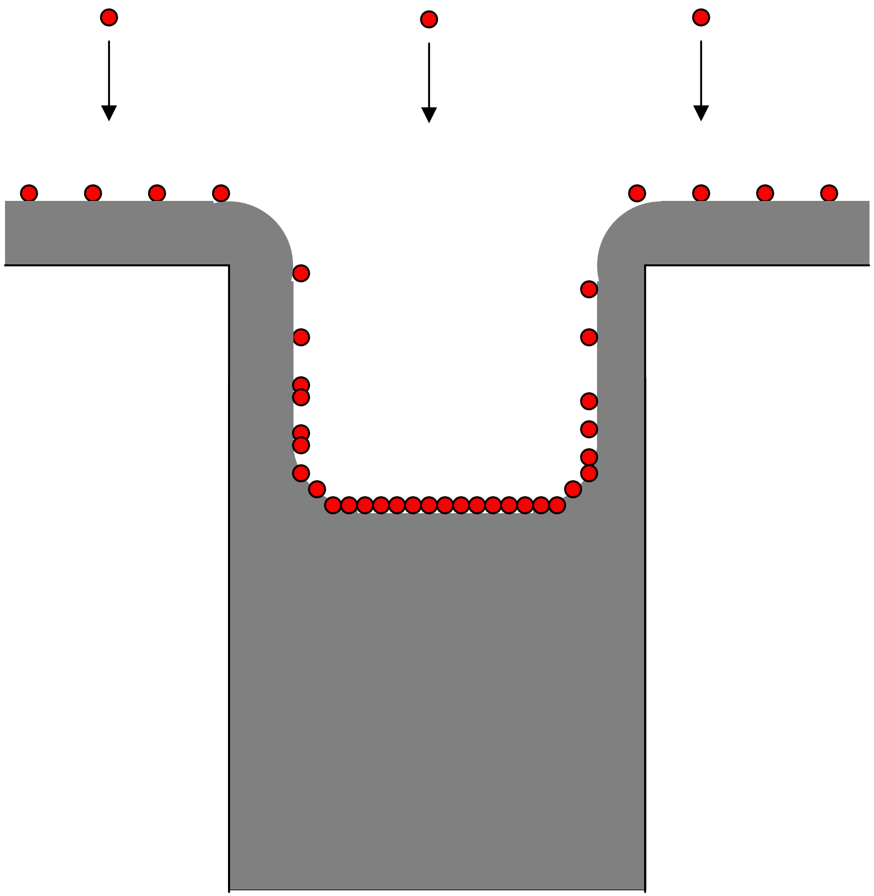
- Catalyst coverage increases on bottom, concave surface, may decrease on top, convex corners.

- Deposition rate highest at bottom of feature.



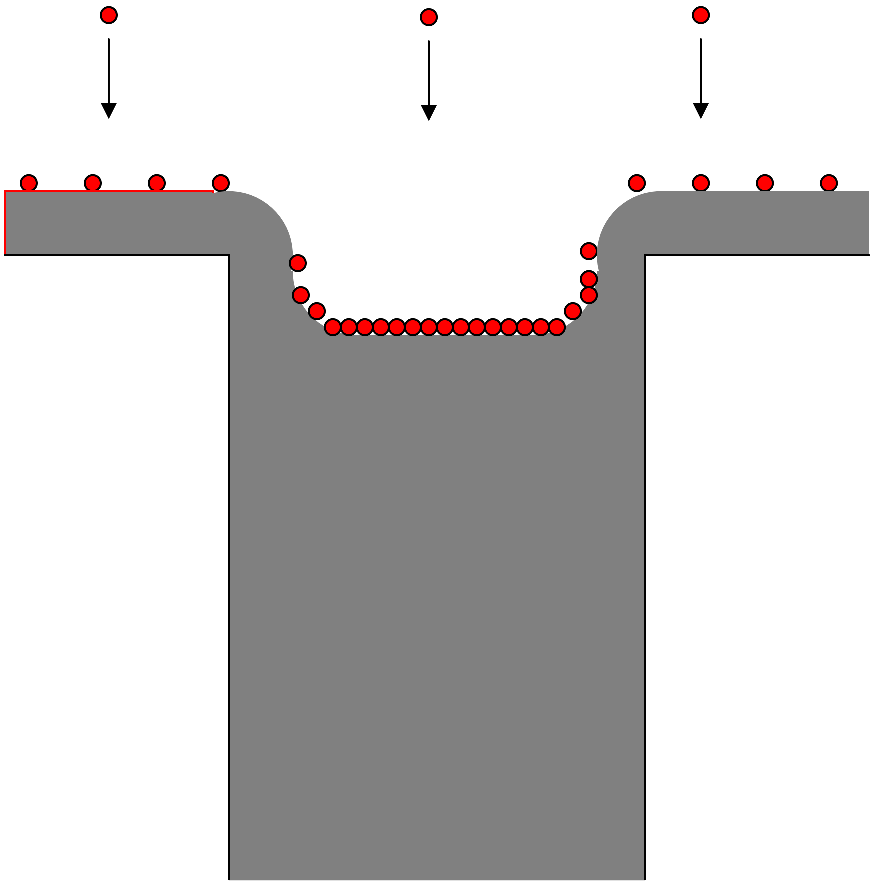
# Curvature Enhanced Accelerator Coverage Mechanism

- Catalyst coverage maximized on bottom surface
- Metal deposition rate at bottom is accelerated.



# Curvature Enhanced Accelerator Coverage Mechanism

- Catalyst coverage maximized on bottom surface.
- Metal deposition is highest on bottom



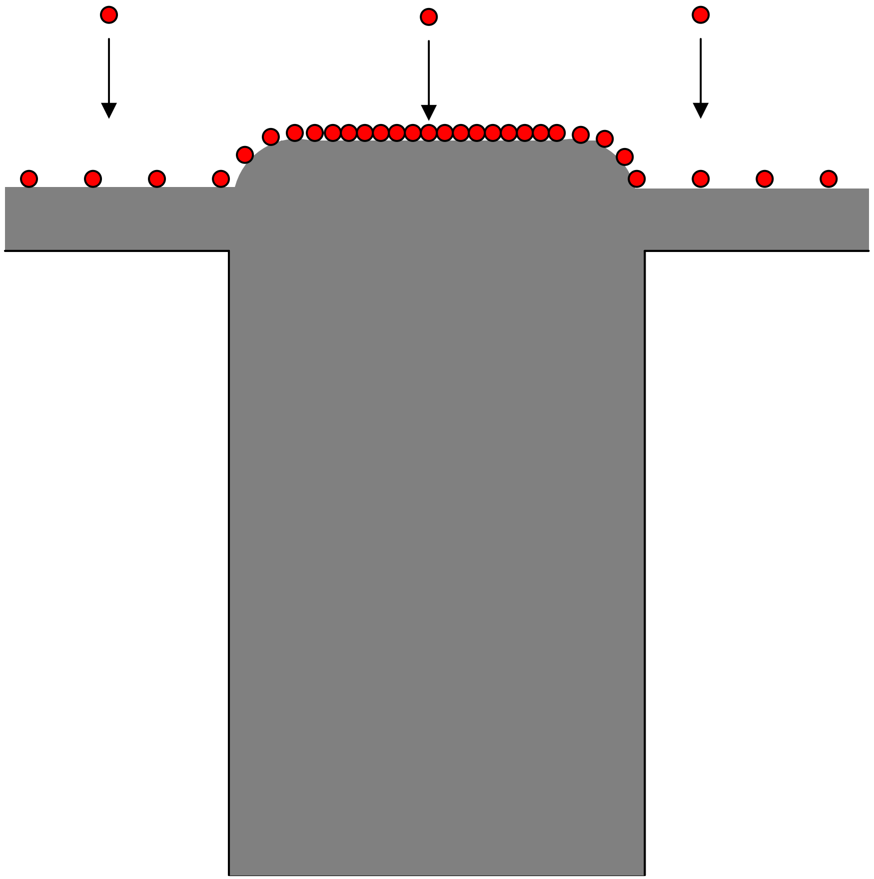
# Curvature Enhanced Accelerator Coverage Mechanism

- Inversion of curvature

  ‘Bottom’ is above trench.

  ‘Momentum plating’

- Catalyst coverage $\theta$ decreases as bump area increases



*Topics:*

- Controlling morphology
- The dual-damascene method
- Electroless deposition
- Multilayer electrodeposition

## *No need for electrical contact to substrate!*

- Conventional electrodeposition:

  electrons that reduce metal ions in solution supplied from external circuit

- Electroless deposition:

  electrons generated at substrate by chemical reducing agent

- Need catalytically active surface

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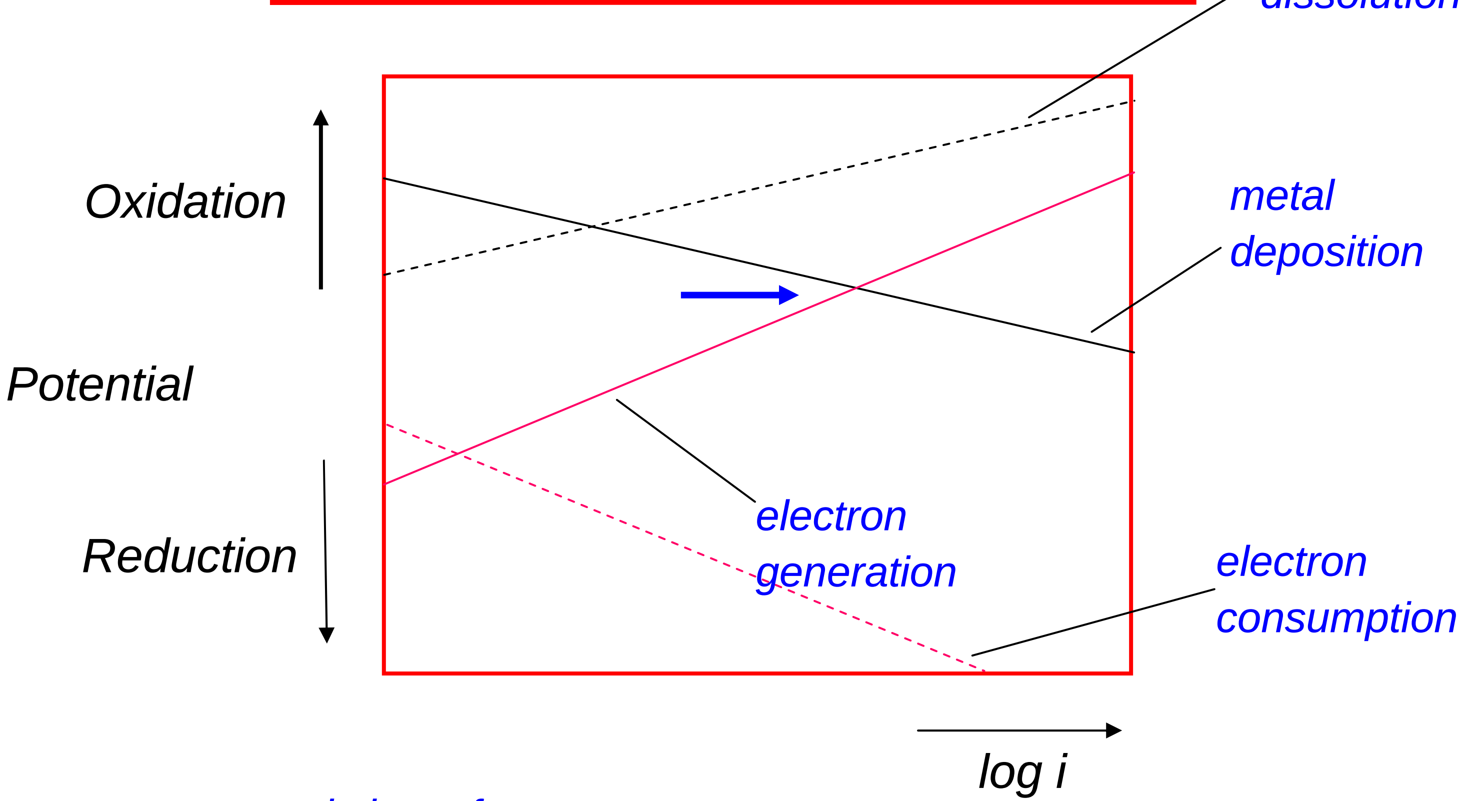
# Example: electroless Cu

*Typical electrolyte: 0.04 M $CuSO_4$, 0.08 M EDTA (ethylenediaminetetraacetic acid - complexing agent), 0.24M HCHO (formaldehyde - reducing agent), 0.4 mM 2,2'-bipyridyl (stabilizer)*

$$2\ HCHO + 4\ OH^- \rightarrow 2\ HCOO^- + 2\ H_2O + H_2 + 2\ e^-$$

$$CuEDTA^{2-} + 2\ e^- \rightarrow Cu^0 + EDTA^{4-}{}_{ADS}$$

# Mixed potential theory




$$M^{z+} + ze \xrightarrow{\textit{catalytic surface}} M_{lattice}$$

$$Re_{solution} \xrightarrow{\textit{catalytic surface}} Ox_{solution} + ne$$

- Electroless deposition can deposit single metals e.g. Cu, Ni, Au or alloys e.g. CoFeB
- Despite versatility, under-exploited in nanotechnology

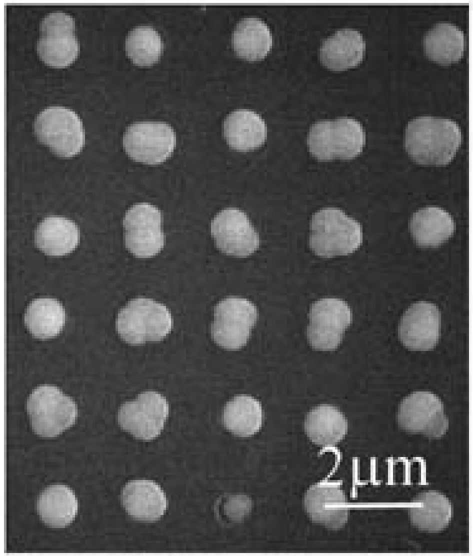



Fig.2 SEM micrograph of nickel dots on silicon wafer.

T.Osaka, N.Takano, S.Komaba; *Chem. Lett*., **7** 657 (1998)

*Topics:*

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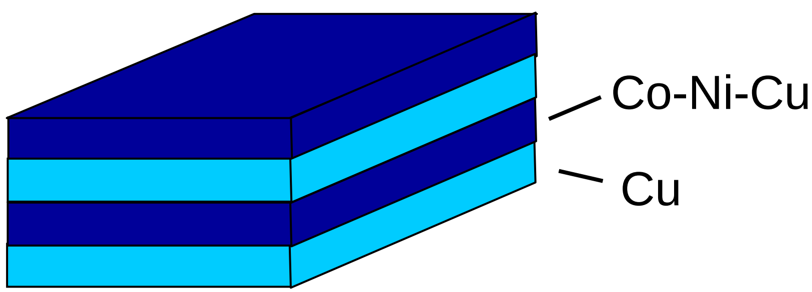
# Multilayer electrodeposition

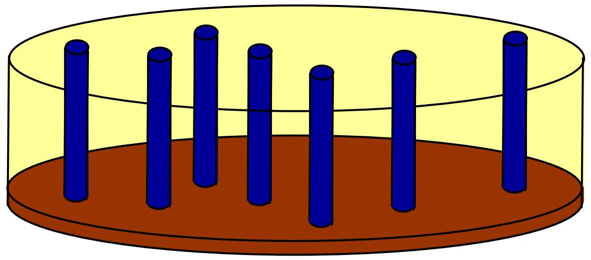
- Use electrolyte containing ions of more than one metal: pulse deposition → multilayer

- Typical example: 0.05M $Cu^{2+}$; 2.3M $Ni^{2+}$; 0.4M $Co^{2+}$
  - -0.2V → pure Cu
  - -1.6V → ferromagnetic Co-Ni-Cu alloy

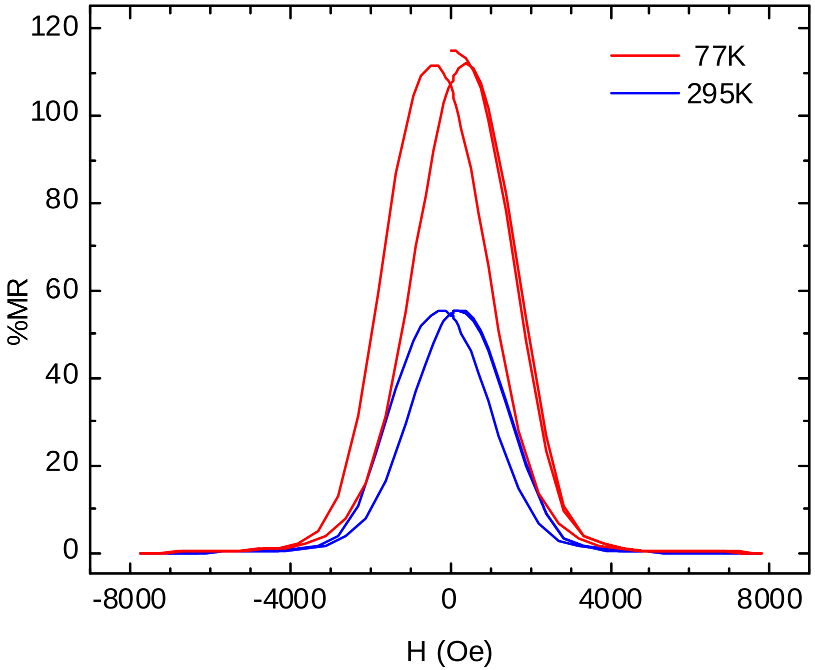


# Multilayer electrodeposition

- For 1-2 nm layers, electrodeposited multilayers show *Giant Magnetoresistance*
- Even greater effect with multilayer nanowires prepared by template deposition:



# Multilayer electrodeposition

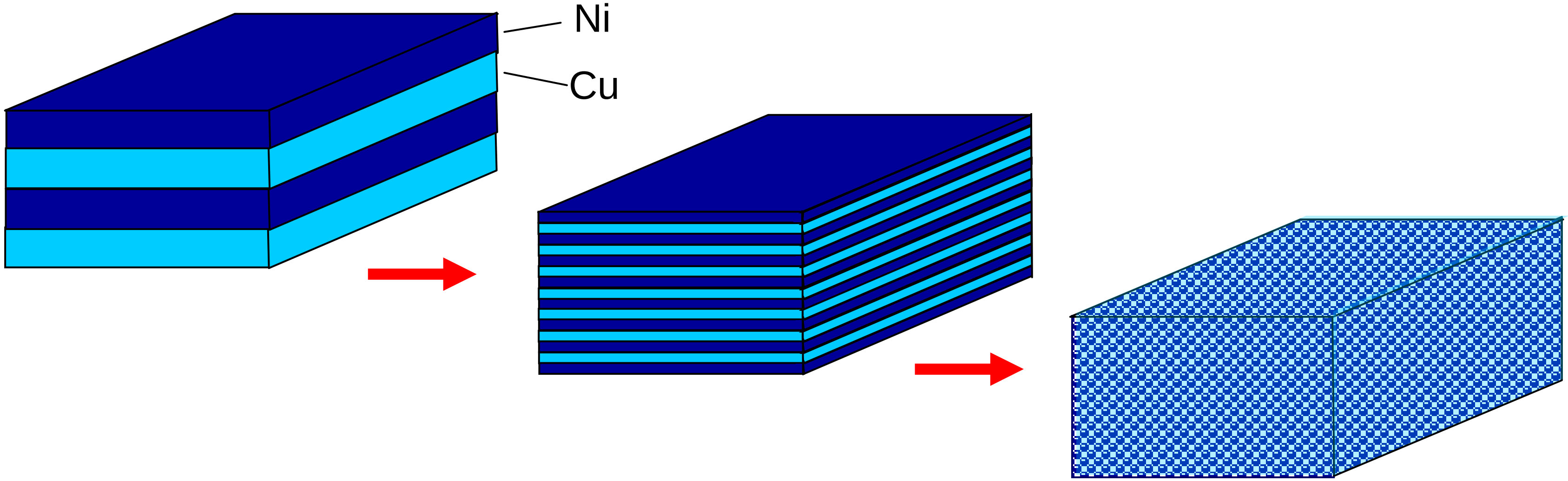




- Over 110% GMR at 77K, over 55% at room temperature

# Multilayer electrodeposition

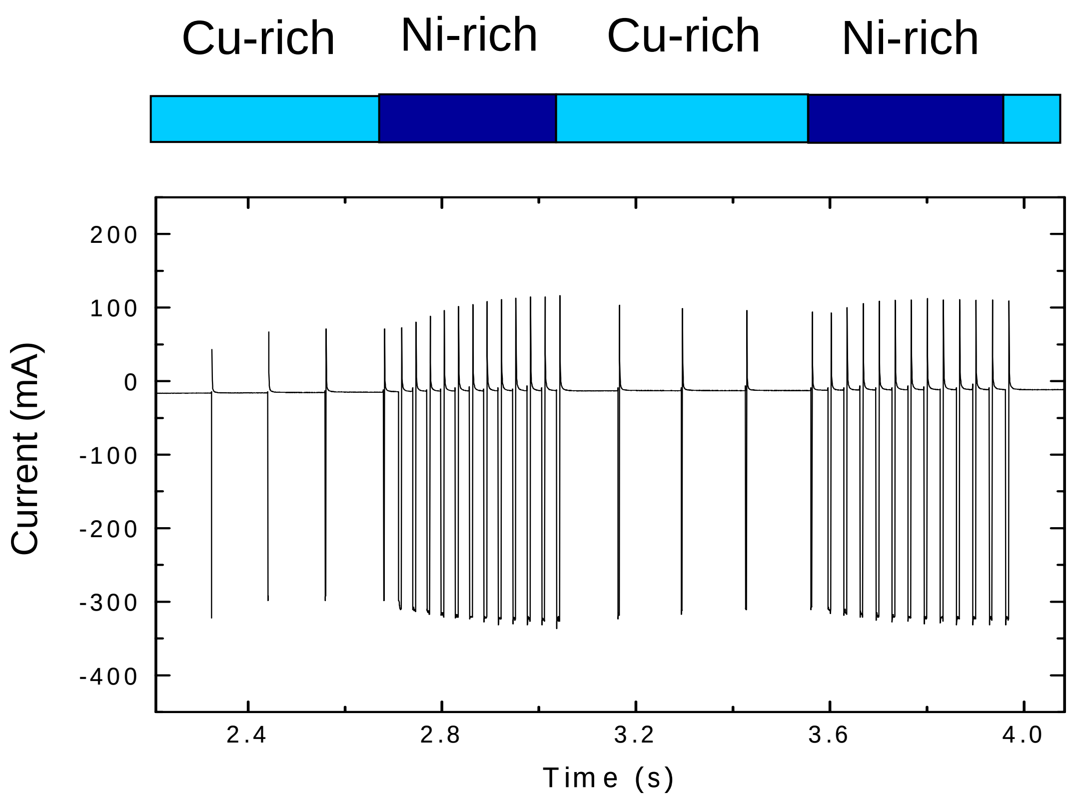
- What happens as layer thickness further reduced?
- Multilayer → heterogeneous alloy




*Electrodeposition Research Group*

# Multilayer electrodeposition

- Can control Cu-Ni alloy composition through lengths of Cu and Ni pulses

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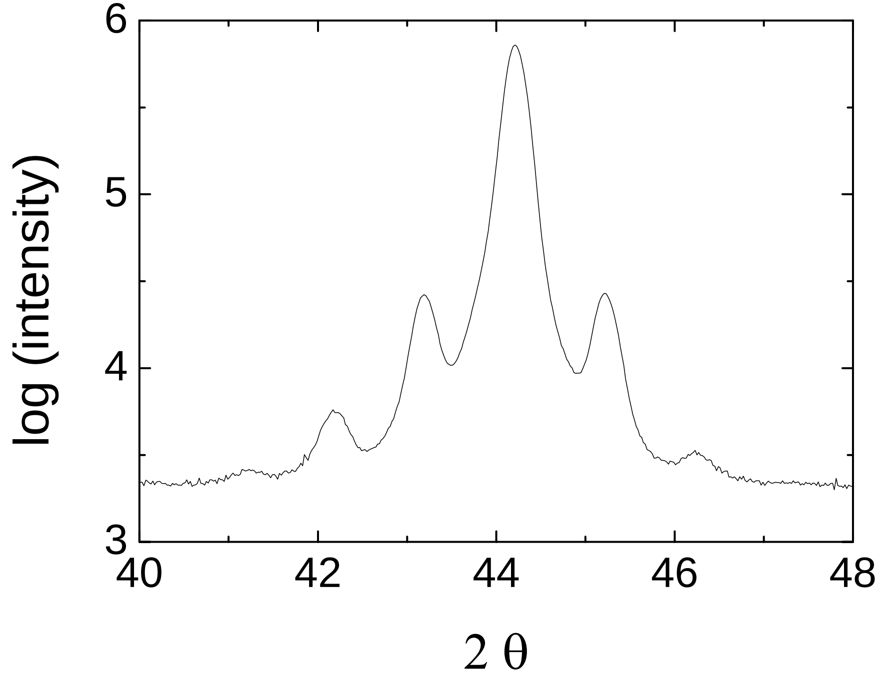
# Application: alloy/alloy superlattice




100×($Cu_{0.19}Ni_{0.81}$ 6nm/ $Cu_{0.79}Ni_{0.21}$ 2nm) alloy/alloy multilayer

# *Acknowledgments:*

S. Huo, J. J. Mallet, R.Cecchini and P. Evans (Bristol)

T. P. Moffat (NIST)


*Disclaimer: the information in this presentation is provided in good faith, but no warranty is made as to its accuracy.*

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